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## **Preparation and Characterization of Green Epoxy Resin Composites and Its Use in Corrosion Resistance**

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### **Abstract**

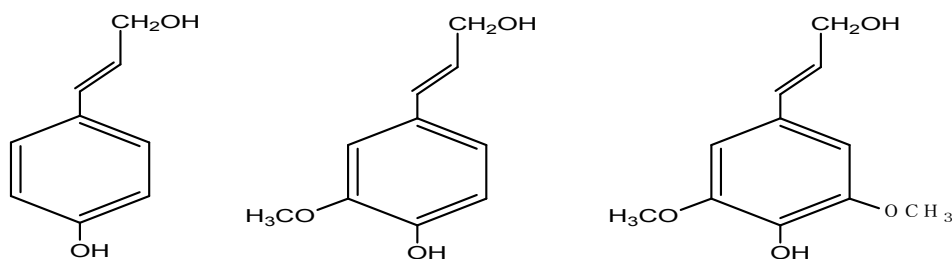
In this work, appropriate alternative for diglycidyl ether bisphenol A (DGEBA) was found to avoid the destructive effects of bisphenol A. Lignin, an aromatic compound from palm tree leaves, was used as a renewable material to synthesize a bio-based epoxy resin. Lignin extracted using Kraft pulping process. Kraft Lignin was epoxidized with epichlorohydrin in alkaline medium. Nano-titanium dioxide was used as filler with ratio of 10% to prepare the green epoxy composite. The structure of the Kraft lignin and lignin-based epoxy resin was proven via Infrared spectra (FT-IR) were recorded using solid KBr disk by testing Shimadzu (FT-IR-8300) spectrophotometer. The thermal properties of the curing process of lignin-based epoxy resin and composite were investigate using Differential scanning calorimetry (DSC) analysis. Potentiodynamic measurements data revealed that the anti-corrosion performance of the lignin based epoxy resin. The study demonstrates successful of epoxidation of Kraft lignin. In addition,

lignin based epoxy resin showed effective inhibitor for carbon steel in 3.5 wt. % NaCl electrolyte solutions.

Keywords: Kraft lignin, Epoxidization, Corrosion inhibitor, DSC

## 1. Introduction

Biomass is a massive promising source of bio-energy and bio-based chemicals that can replace fossil oil. Thus, this material is important in sustainable production because it is renewable and abundant resource on Earth. Lignin is a complex phenolic polymer that is present in plant tissues. This most abundant and important natural polymer on earth second to cellulose is a byproduct of the pulp and paper industry [1,2]. Lignin is described as an amorphous three-dimensional network. The repeated units in the formation of this complex polymer are phenylpropanoid monomers, namely, sinapyl, and *p*-coumaryl alcohols [2,3].



**Figure 1:** Three main phenylpropanoid units of lignin: (a) *trans-p*-coumaryl alcohol, (b) *trans*-coniferyl alcohol and (c) *trans*-sinapyl alcohol

The bio-structure of lignin is made of the free radical reaction of these monomers to form a stiff, three-dimensional cross-linked matrix (very similar to thermosetting resins such as phenol-formaldehyde resins), these structures need a high flexibility towards the rearrangement of bonds within the lignin network, which leads to more condensed polymers. Chemically, lignin is considered a complex insoluble biopolymers, although many studies have been conducted, its chemistry and molecular biology is still not completely understood [4]. A wide range of functional groups are characterized in lignin. These groups are capable of meeting industrial requirements. The effectiveness of lignin mainly depends on the aliphatic and phenolic hydroxyl groups, as well as the carboxyl groups. The solubility of lignin depends largely on the percentage of these functional groups. Generally, most types of lignin are quite soluble in alkaline solutions as a result of the ionization of carboxyl and hydroxyl functional groups [5]. In the aromatic rings on lignin, only about 10–13% of the phenolic hydroxyl groups are free to form neighboring phenyl propane linkages, whereas the others form ether linkages [5]. The phenols content is important because it has a major role in chemical reactions, especially in modified lignin because it is the most reactive site in lignin structure. Lignin can be regarded as a raw material for various applications. The opportunities and challenges of the use of lignin were described in an extensive study [6]. There are many literatures exhibit that lignin and epoxy (DGEBA) resin mixture is used to producing printed electric boards and it which content of lignin up to 60% have shown good electrical and physical properties. In thermoset composites, lignin were used to increase toughness and stiffness [7,8,9] and lignin was also was found to increase the flexural strength in flax-epoxy composites [10].

Due to health and environmental risks, recently research efforts have been focused on the development of sustainable monomer and polymer alternatives [11,12]. In this study, Kraft Lignin that extracted from palm tree leaves was used for the preparation of bio-epoxy resin composites instead of the diglycidyl ether bisphenol A (DGEBA).

## **2. Materials and Methods**

### **2.1. Materials**

The palm tree leaves (PTL) that was used for delignification was supplied by local plantation in Yusufiyah, Iraq in 2014. Sodium hydroxide (NaOH), sodium sulfide (Na<sub>2</sub>S) and ethanol were obtained from QREC (ASIA). Formaldehyde was supplied by HmbG Chemicals. Epochlorohydrin was purchased from Merck (Germany). Titanium dioxide (TiO<sub>2</sub>) was obtained from Riedelde Haen (product code: 14027), Germany, The purity of titanium nano particles was  $\geq 99.5$  and average particle size around 10-30 nm.

### **2.2. Characterization**

Infrared spectra (FT-IR) were recorded using solid KBr disk by testing Shimadzu (FT-IR-8300) spectrophotometer, and in terms of the number of wave form (400-4000) cm<sup>-1</sup> range. Differential Scanning Calorimetry (DSC) of the compounds was carried out by Linseis (STA TT-1000) instrument. Corrosion resistance were measured by Galvanostatic test by using potential static device and potential were recorded (mV) and

current were recorded (nA,  $\mu$ A)/cm<sup>2</sup>. All tests were conducted at department of Materials Research, Department of Research and Development Industrial/Department of corrosion - Ministry of Science and Technology.

### 2.3. Kraft pulping

Kraft lignin (KL) was recovered as a byproduct from PTL using Kraft pulping process. The air-dried PTL were ground to 20 mesh using a ball mill. The PTL were dried at 105 °C in an oven prior to the Kraft pulping process. The mass ratio between dried PTL and the used solvent (sodium hydroxide and hydrous sodium sulfide) was 1:8. The 1 L stainless steel reactor was loaded with 44 g of (PTL), 19% sodium hydroxide and 25% of hydrous sodium sulfide. The temperature of cooking was set from room temperature to 170 °C for 3 h. After cooking, the solid and solvent fractions were separated using a filter paper and washed with distilled water and the black liquor was collected.

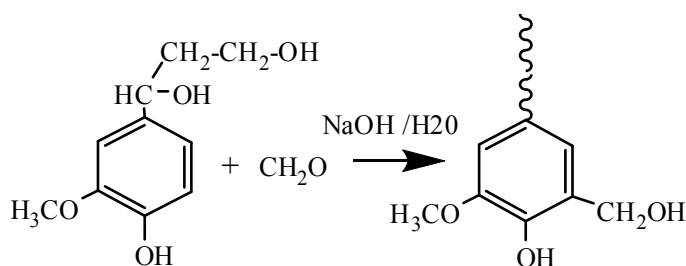
### 2.4. Kraft lignin extraction (KL)

The Kraft black liquor has a pH of 12.5. KL was precipitated from the concentrated black liquor by acidification using 20% (v/v) sulfuric acid (pH 2) [13]. KL was filtered and washed with distilled water at pH 2 and then dried in a vacuum oven at 45 °C for 48 h.[14]. The KL was purified by extraction it in a soxhlet apparatus for 6 h with *n*-pentane to remove the lipophilic non-lignin matters, such as wax and lipids. This step was followed by filtration and washing the product using distilled water (normalized at pH=2) to remove excess *n*-pentane and non-lignin phenolic compounds that may have remained

after the pulping process. The purified KL was dried in a vacuum oven at 45 °C for 48 h. Then KL was treated with hot water to dissolve the residual sugars [15]. Finally, the obtained lignin was again dried in a vacuum oven at 45 °C for 48 h.

## 2.5. Preparation of Methylolic Kraft lignin (MKL)

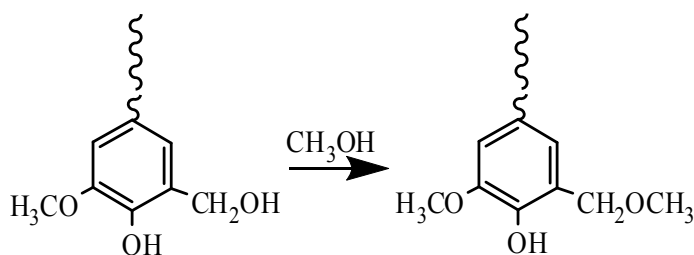
Kraft lignin powder (1.5g) was slowly added to 10% of NaOH aqueous solution, keeping the PH of the mixed solution between (11-12) for better dissolution of the Kraft lignin powder. This mixture was placed in a 250 mL flat bottom flask equipped with a condenser, thermometer and magnetic stirring bar and heated to 60 °C. A quantity of (5) ml from formaldehyde was added with a magnetic stirrer on a hot plate for 8 hours. The mixture was cooled at 3 °C. The reaction mixture was neutralized, using 10% (v/v) of alcoholic phosphoric acid, until neutralization pH=7. The reaction mixture was filtered, recrystallized and dried. The MKL was prepared as shown in scheme 1. Some physical properties for this compound were listed in Table 1.



**Scheme 1:** Synthesis of Methylolic Compound

## 2.6. Preparation of Saturated Etheric Compound

The 0.2 mol of saturated alcohol (Methanol) with 0.5 mL of sulfuric acid were mixed at 5 °C, then 0.2 mol of a Methylolic Compound was added gradually with stirring at room temperature for 1 h with the rise of the temperature to the boiling point of the alcohol used. The reaction mixture was refluxed for 24 h. Then cooled, the mixture was neutralized with sodium hydroxide. The reaction mixture was filtered, recrystallized and dried. The reaction of methylolic compound and methanol was illustrated in scheme 2 and physical properties for this compound were listed in table (1).



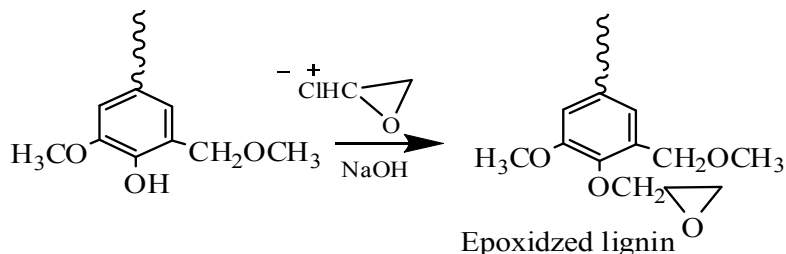
**Scheme 2:** Synthesis of Etheric compound

## 2.7. Epoxidization of Etheric Compound

The Kraft lignin based epoxy resin (KLER) was prepared from the reaction between the 1g of the Etheric compound and 30 mL of epichlorohydrine. The reaction mixture was mixed with 10 mL of butanol for 15 mins at 50 °C, and then gently added 2g of sodium hydroxide in two stages while maintaining temperature below 70 °C. The mixing continues for 3 h. After the first addition the aqueous layer was separated from the organic layer, and then a second batch of sodium hydroxide was added and mixed for 1 h.



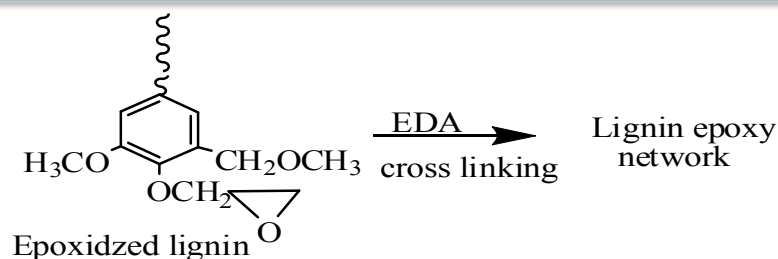
The aqueous layer was separated while the organic layer was dried and recrystallized. Epoxidization of Etheric compound as shown in scheme 3. Physical properties for this compound were listed in table (1)



Scheme 3: Epoxidization of Etheric compound

## 2.8. Lignin based epoxy system preparation Compound

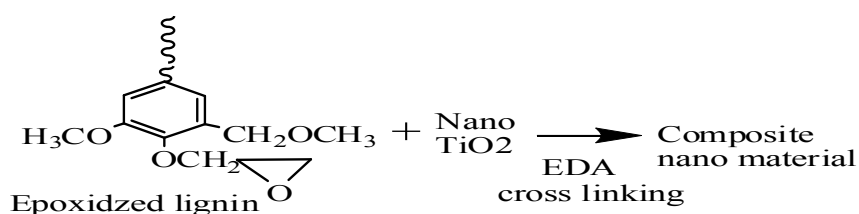
1.5 g of the epoxidized Kraft lignin compound was mixed with 0.5 g of ethylene diamine (EDA), which used as a curing agent .The mixing ratio of the two parts was 3:1. The gelation time of bio epoxy system was 45 minute at 35 °C, mixed viscosity 1.18 poise at 35 °C and complete cured at 35 °C was 10 days. Scheme 4 illustrates the preparation of a lignin-based epoxy resin network. Physical properties for this compound were listed in table (1).



**Scheme 4:** Synthesis of lignin-based epoxy resin network

## 2.9 Lignin-based epoxy resin composite Compound

Kraft lignin-based epoxy resin composite was prepared by mixing of 10 % weight ratio of nano titanium dioxide. (TiO<sub>2</sub> in KL-based epoxy resin and then added EDA as a curing agent. Bio-epoxy resin composite was prepared as shown in scheme (5). Some physical properties for this compound were listed in table (1).



**Scheme 5:** Synthesis of Lignin-based epoxy resin composite Compound

**Table 1:** physical properties of compounds (1-5)

No	Compound	Colour	Yield %	Purify- Solvent
1	Methyloic Compound	Grey	65	Distilled water
2	Saturated Etheric	Grey	60	Ethanol

	compound			
3	Epoxidization of lignin	Dark Grey	70	Ethanol
4	Lignin epoxy net work	Grey	77	Ethanol
5	Composite nanomaterial	Dark Grey	55	THF

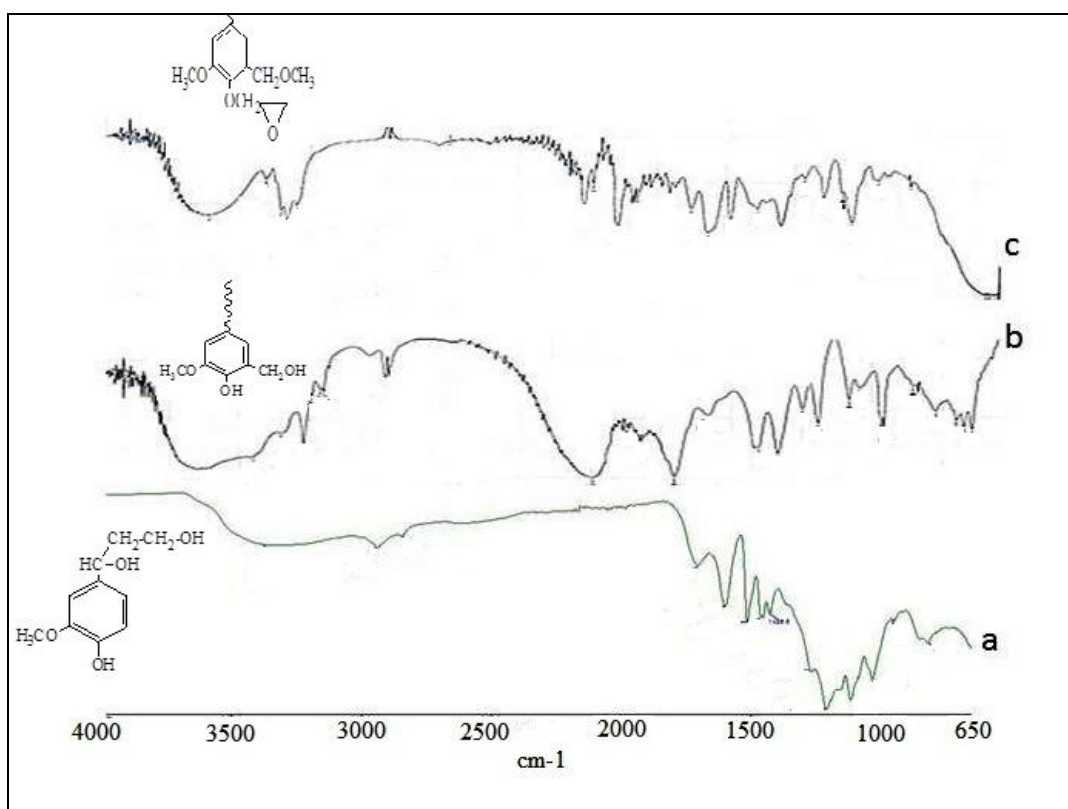
### 3. Results and discussion

#### 3.1. FTIR spectroscopy

Fourier transform infrared spectroscopy (FTIR) was used to determine the change that occurs in the functional groups of the lignin compounds and their derivatives. The FTIR spectra of the KL, Methylolic compound (MKL) and the KLER samples are shown in figure 1 respectively. The assignments of KL spectrum are consistent with previous report [16]. A large band at  $\sim 3327\text{ cm}^{-1}$  was assigned to phenolic and aliphatic OH stretching vibrations and peaks around  $2937$  and  $2839\text{ cm}^{-1}$  were attributed to CH stretching in the methyl and methylene groups in the side chains and aromatic methoxy groups. These signals also appeared in methylolic and KLER samples. Bands at  $1512$ ,  $1452$ , and  $1423\text{ cm}^{-1}$  are attributed to aromatic ring vibrations of the phenyl-propane (C9) skeleton. The absorption band attributed to C–O stretching in a plane deformation is located at  $1365\text{ cm}^{-1}$  of KL, whereas this signal was shifted from methylolic and KLE samples in  $1267$  and  $1247\text{ cm}^{-1}$  respectively.

Compared to KL, FTIR spectra of MKL and KLER reveal important increase in peaks intensity: at  $\sim 1068\text{ cm}^{-1}$  and  $\sim 1184\text{ cm}^{-1}$ , assigned to aliphatic C–OH groups and ethers

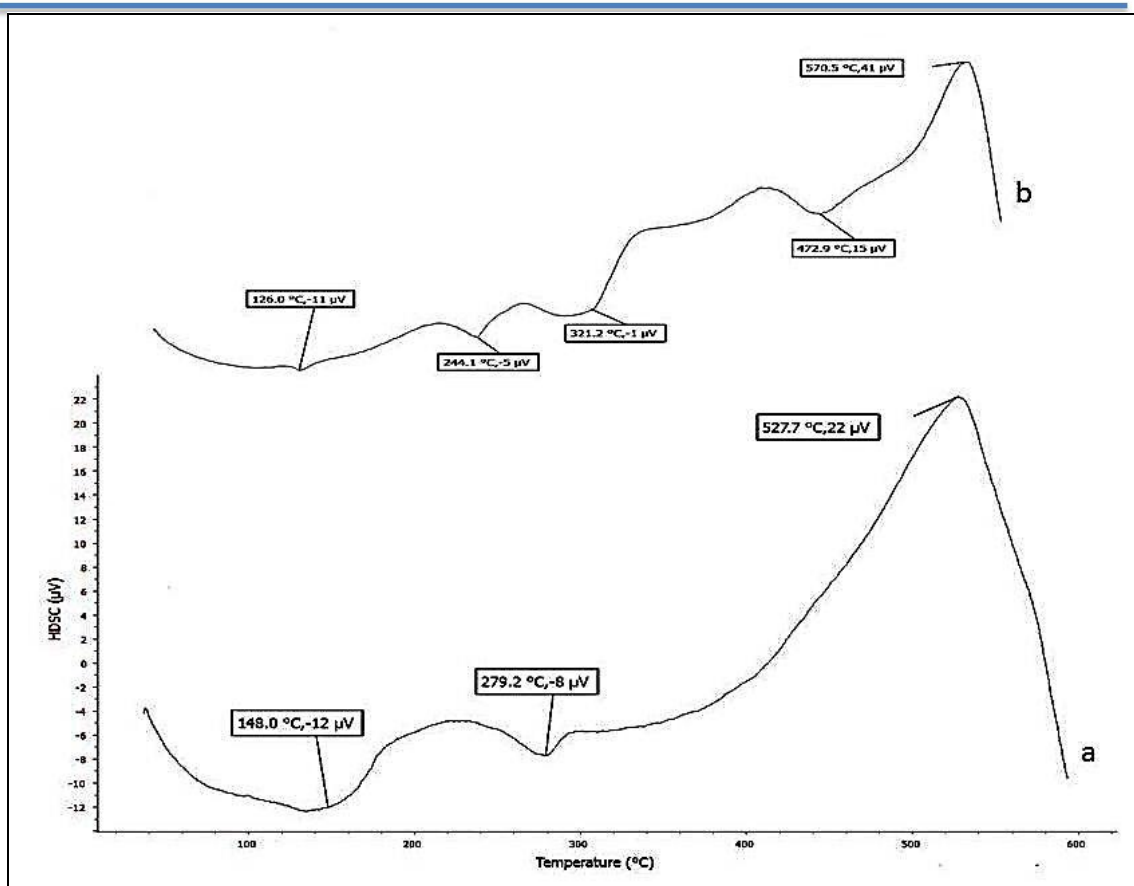
(C-O-C) groups (compared with a small peak in Kraft lignin at  $\sim 1030\text{ cm}^{-1}$ ), at  $\sim 2872\text{ cm}^{-1}$  (aliphatic CH bonds). The significant increase in this peaks intensity can be attributed to the structure of methylolic compound. The significant increase in these peaks intensities can be attributed to the structure of PEG and glycerol. The MKL reveal that the absorption intensity of methyl groups significantly increased in the new bands at  $\sim 2831\text{ cm}^{-1}$ . The appearance of new absorption bands at  $831$  and  $916\text{ cm}^{-1}$ , due to epoxy group, known as (oxiranes or alkylene oxide) which attack on the phenolic  $\nu$  (OH) group. These signals seem to confirm that KLER was synthesized through the reaction of EKL and epichlorohydrin.



**Figure 2:** FT-IR spectrum of (a) KL, (b) MKL and (c) KLER

### 3.2. Thermal properties of lignin-based epoxy resin

DSC provides useful information about the curing conditions of epoxy systems and many studies have been performed on the epoxy resin to obtain kinetic data using DSC analyses [17,18,19]. Generally, the curing reaction of epoxy resin is an exothermic behavior. Therefore, DSC analysis can determine whether the epoxy resin was cured, depending to the heat change in epoxy resin blends. The DSC thermo gram shows two samples in Figure 2. In the range of 30-600 C, the DSC curve of the methylolic compound (MKL) does not appear any exothermic peak confirming that there was no chemical reaction between hydroxyl and carbonyl groups to liberate volatile compounds. In contrast, epoxidized samples (KLER) showed exothermic peak in the range of 320-425 C. This might be ascribed to the cross-linking of curing reaction of the epoxidized sample with ethylene diamine (EDA) and opening of epoxy ring via amine groups, thus the heat will be released.

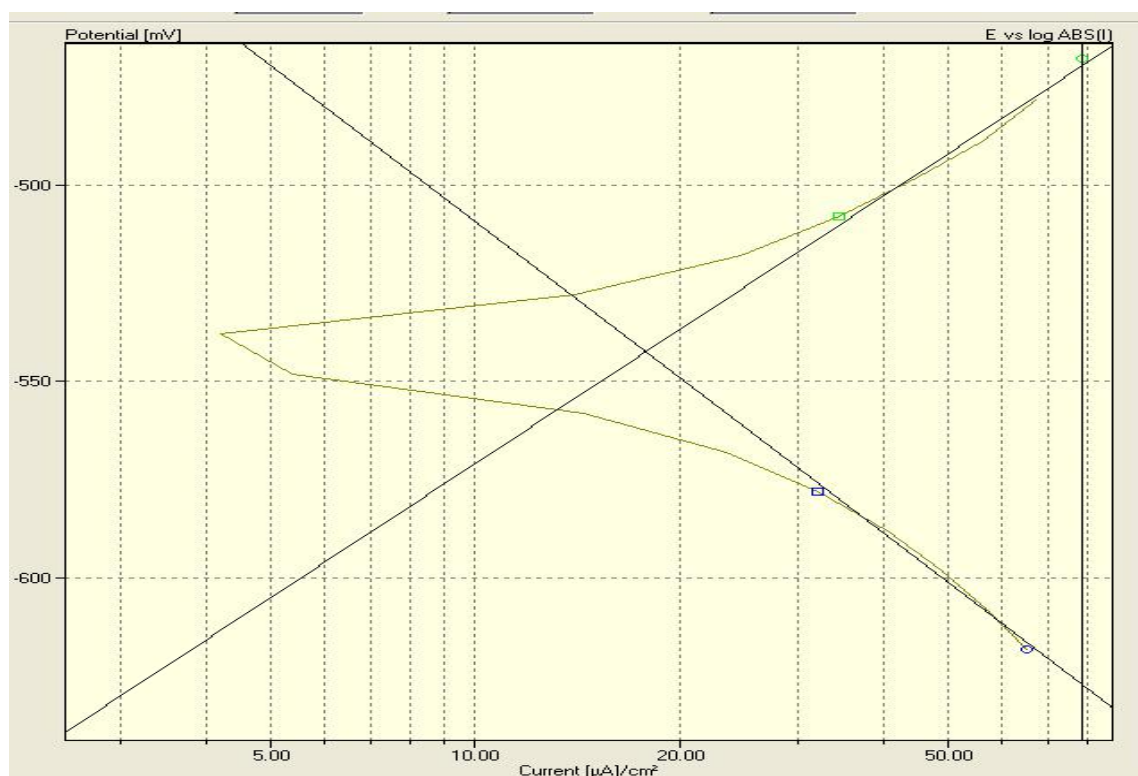


**Figure 3:** DSC of (a) KLE and (b) MKL

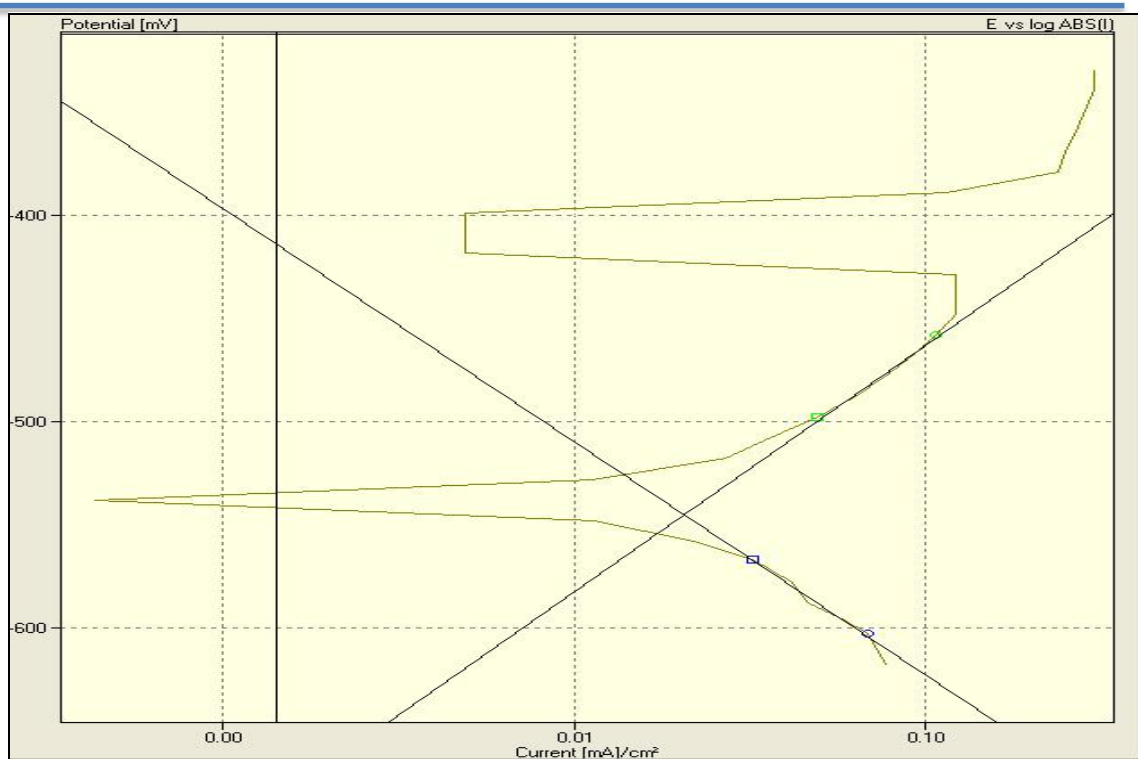
### 3.3. Potentiodynamic measurements

The Potentiodynamic measurements are highly relevant and widely utilized to estimate the electrochemical activity of corrosion protection coatings for metal. The corrosion behavior was characterized at 35 °C by Galvanostatic tester and the samples were evaluated in 3.5 wt. % NaCl electrolyte solution at room temperature by using Potential Static Device, with pH adjustment to 4.5 in order to determine the corrosion rate. Evaluation of corrosion protection properties for protective coatings of Lignin based

epoxy resin might be used tafel plots to determine of important parameters such as corrosion current ( $I_{corr}$ ). The current corrosion of the carbon steel metal was recorded when immersed in the salt water (3.6% NaCl) solution before doing the paint process and record the current corrosion ( $I_{corrosion}$ ) about  $(78.7) \mu A / cm^2$ , Figure (4). Epoxidization of lignin compound, Figure (5), shows corrosion resistance and record the current corrosion ( $I_{corrosion}$ ) about  $(1.4) \mu A / cm^2$ . The Epoxidization of lignin and nano  $TiO_2$  (10%), Figure (6), showed resistance to corrosion and record the current corrosion ( $I_{corrosion}$ ) about  $(184.0) nA / cm^2$ .

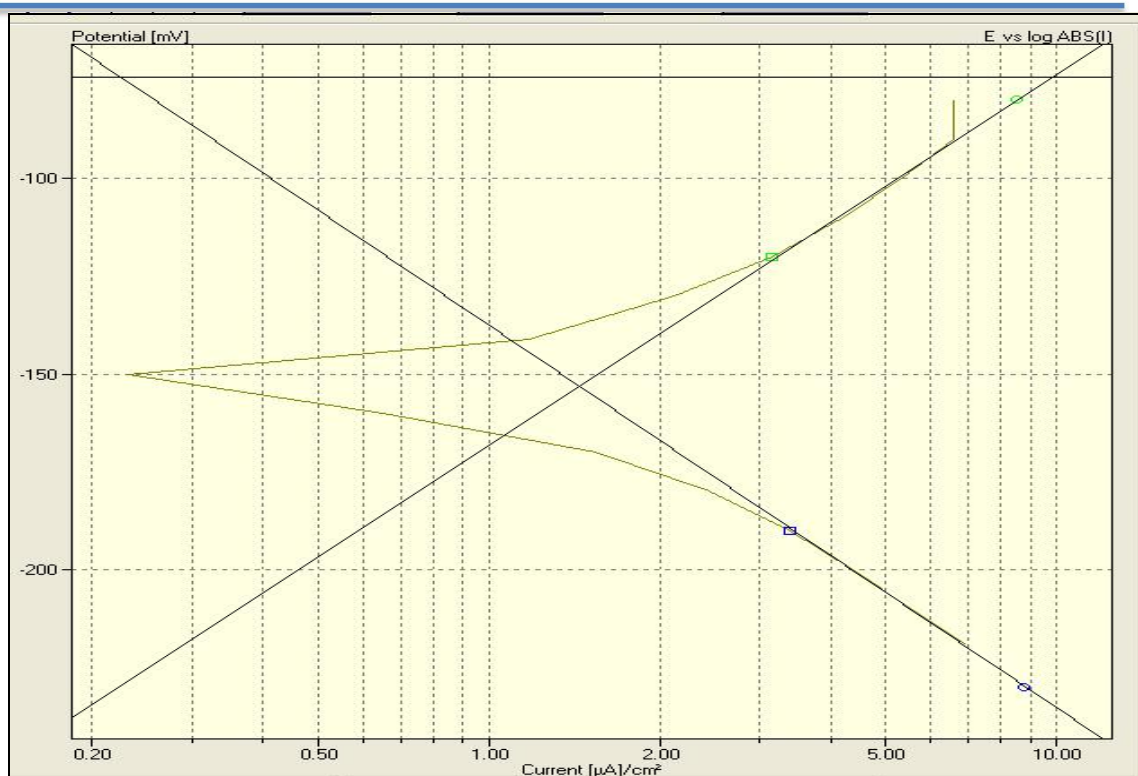


**Figure 4: Polarization curve of carbon steel**



**Figure 5: Polarization curve of KLER**





**Figure 6:** Polarization curve of KLER and nano TiO<sub>2</sub> (10%)

#### 4. Conclusions

In summary, the Kraft lignin was modified to be used as a bio-based epoxy resin via reaction with epichlorohydrin. Towards to this end, Kraft lignin was firstly converted to Methylolic compound and then to the saturated etheric compound through a reaction with sodium hydroxide and methanol respectively. Chemical structure of KL, MKL and KLER was successfully confirmed by FTIR analysis. The results of DSC analysis showed that the KLER presented exothermic peak in the range of 320-425 C, confirming cross-linking reaction has been happened of epoxidized sample and ethylene diamine (EDA). The corrosion studies of KLER composite (10% nano TiO<sub>2</sub>) shows lower rate of corrosion than pure KLER when paint process of carbon steel.

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